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Narrower Bands with Better Charge Transport: the Counterintuitive Behaviour of Semiconducting Co-Polymers

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Organic polymeric semiconductors have been studied extensively for almost 30 years because of their potential applications and, in principle, the ability to fine tune their properties via chemical synthesis.^[1] However, the relation between their chemical structure and charge mobility is far from clear. The best materials seem to belong to different classes (semicrystalline polymers^[2-3] or amorphous “aggregating” polymers^[4-5]) and there is little guidance that theory has been able to offer to help the design of new materials. It is also surprising, from a purely physical point of view, that polymers with an extremely simple structure and a wide band like PPV (polyphenylene vinylene)^[6] are orders of magnitude worse in terms of charge mobility compared to recently introduced copolymers that display a very complex chemical structure and, apparently, a lower degree of electronic conjugation (and narrowed bandwidths) due to their greater flexibility. Although the charge transport does not take place via band transport, narrow bandwidths are considered detrimental to transport in the most common models of transport used for polymeric semiconductors. In variable range hopping models narrower bands cause greater localization and slower hopping rate and, in mobility edge models, they cause the reduction of the mobility of carriers outside the traps. In this letter we discuss how a more complicated electronic structure with narrower band can instead improve the mobility.

The starting point of our analysis is that the difference between good and bad polymers is the degree of disorder as illustrated almost conclusively by recent ref. ^[7], where a large number of polymers has been considered, and in agreement with a long series of previous works.^[8] A consequence of this observation is that the localization of the states available to the charge carrier is determined by the electronic disorder and not by the electron phonon coupling, a conclusion that seems to represent the consensus in the area^[9-11]. Calculations of long polymer chains in conformations obtained from molecular dynamics simulations suggest that the main cause of localization of the orbital in single polymer chains is the variation (disorder) in the dihedral angles of the conjugated backbone, in the 15°-35° range for different polymers, which causes a variation of the electronic coupling between monomers corresponding to 5-20% of the average coupling.^[12-14]

Therefore, we start considering a purely electronic disordered Hamiltonian (the effect of electron-phonon coupling will be discussed later) with one state $|i\rangle$ per site i (representing a monomer) and nearest neighbor coupling:

$$H_0^{el} = \sum_i \alpha_i |i\rangle\langle i| + \sum_i \beta_i |i\rangle\langle i+1| + h.c. \quad (1)$$

To represent a copolymer structure with alternating sites of different energy, we set $\alpha_i = \Delta/2$ for odd values of i and $\alpha_i = -\Delta/2$ for even values of i . β_i is a random variable distributed normally around an average value β with standard deviation σ_β . We have chosen in the main manuscript to consider only the disorder in the off-diagonal terms, following the indications from our atomistic studies^[13] that this is the main term determining charge localization and DOS. The results, however, remain similar if a realistic on-site disorder is added to the model, as shown in detail in the SI, where additional results with on-site disorder are included. Using different realizations of the disorder and a chain of 1000 sites we have computed the density of states (DOS) of the model from the eigenvalues E_j^0 of H_0^{el} as $DOS(E) = \sum_j \delta(E - E_j^0)$. For each eigenvector c_{ij}^0 we evaluated the localization length as $LL_j = 2 \left[\langle \psi_j^0 | r^2 | \psi_j^0 \rangle - \langle \psi_j^0 | r | \psi_j^0 \rangle^2 \right]^{1/2}$ and we have derived an average energy-dependent localization length as $LL(E) = DOS(E)^{-1} \sum_j LL_j \delta(E - E_j^0)$. $DOS(E)$ and $LL(E)$ for different values of the parameters Δ/β and σ_β/β are given in Figure 1.

In the absence of disorder ($\sigma_\beta/\beta = 0$) and for the homo-polymer (i.e. when all monomers have the same energy and $\Delta/\beta = 0$) the DOS is obviously that of a one-dimensional chain and the states are fully delocalized. For $\Delta/\beta \neq 0$ the system develops two bands which for $|\Delta| > \frac{1}{2}|\beta|$ contain states in two separate energy regions. The wavefunctions in the low energy band have their probability density concentrated on the sites corresponding to the low energy monomer and vice-versa. These bands are similar to that of a one-dimensional chain with a smaller effective coupling: two donors separated by an acceptor are not directly coupled but their wavefunction is mixed because they are both coupled to the same acceptor. The effective coupling between two degenerate sites mediated by another bridge site at different energy (known as superexchange^[15]) decreases with increasing the energy gap (Δ) between the sites that are coupled and the site that mediates the coupling. The parameter Δ controls both the energy separation between the bands and their narrowing. In the absence of disorder, the eigenfunctions are fully delocalized, i.e. $LL(E)$ are of the order of the size of the system.

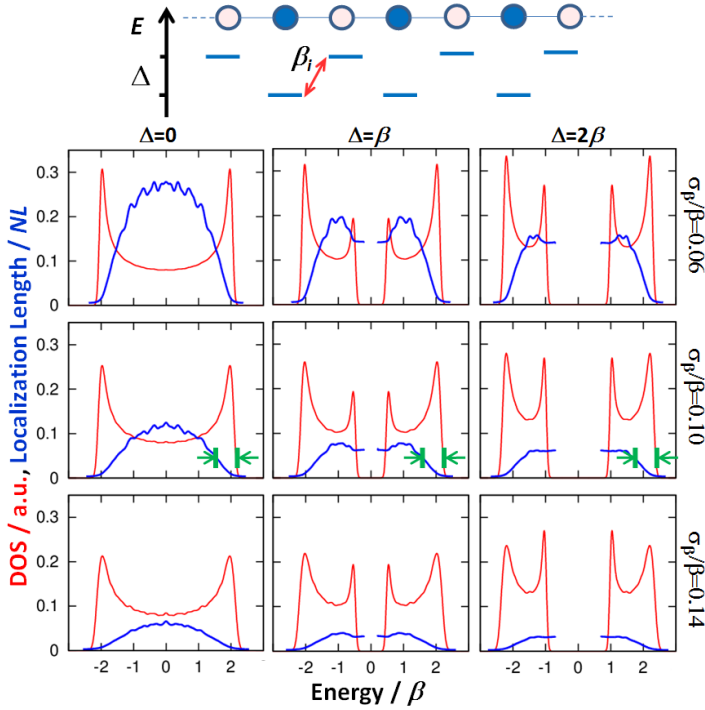


Figure 1. (top) A cartoon representing the model Hamiltonian considered in this work. (bottom) Nine panels representing the DOS and localization length for the model system for different choices of disorder (σ_β / β) and difference of on-site energy (Δ / β). Arbitrary energy intervals shown in green in the central panels illustrate that the activation energy between localized states at the band edge and delocalized states within the band may be similar. A rigorous definition of the activation energy can only be achieved via the model discussed in main text (results shown in Figure 2).

Introducing disorder, i.e. when $\sigma_\beta / \beta_0 > 0$, few expected changes occur regardless of Δ : the DOS is broadened and the localization decreases. Importantly, as noted for example in ref. ^[13], the states at the band edge are more localized than the states deeper in the band. According to the mobility edge model,^[16] charge mobility is thermally activated because very localized states in the tail of the band are not mobile while states deeper in the band have higher mobility and the measured thermal activation is the typical energy required to de-trap the carrier from the band tail. Actual calculations of model Hamiltonians^[17-18] do not display a sharp cut-off between localized and delocalized states, but a similar principle may be in action, with higher temperatures increasing the population of charge carriers at more delocalized and therefore higher mobility energies. The central hypothesis of this work is that the activation energy required to promote charge carriers from localized states in the band tail to delocalized states deeper in the band is *reduced for narrower bands*, simply because they are narrower and delocalized states are therefore closer to the band edge. This hypothesis would explain why the activation energy for transport is reduced for co-polymers (being everything else the same). Narrow bands, however, imply weaker coupling between localized states so one has to evaluate the combined effect of having more delocalized states closer to the band edge (which

would increase the mobility) and a reduced coupling between these states (which would decrease the mobility).

To make the argument more quantitative, we adapt a recent model proposed to describe the mobility of a single polymer chain in the presence of static disorder, dynamic disorder and electron-phonon coupling.^[17] We consider the Hamiltonian:

$$H(p_i, x_i) = H_0^{el} + H^{nucl} + V^{el-nucl} + V^{el}(t) \quad (2)$$

where H_0^{el} is the electronic Hamiltonian of eq. 1. One effective nuclear degree of freedom is assumed to be present per monomer, harmonic and linearly coupled with the electronic degrees of freedom (x_i, p_i, m, ω and g are displacements, momenta, effective mass, effective frequency and electron-phonon coupling parameter respectively):

$$H^{nucl} + V^{el-nucl} = \sum_{i=1,N} \frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 x_i^2 + \sum_{i=1,N} g x_i |i\rangle\langle i| \quad (3)$$

As a result of the coupling with the thermal bath, a random fluctuation of the inter-monomer coupling is included in the model. This is described by the time dependent coupling $\gamma_i(t)$, characterized by $\langle \gamma_i(t) \rangle = 0$ and $\langle \gamma_i(t)^2 \rangle = G^2$, and the Hamiltonian term

$$V^{el}(t) = \sum \gamma_i(t) |i\rangle\langle i+1| + h.c \quad (4)$$

The coupling in eq. 4 parameterizes the non-adiabatic coupling^[19] and it is equivalent to the coupling considered in ref. ^[20] if the thermal bath motions can be considered classically. In this limit, and within the remaining assumptions of the model, there is no difference between one or more effective nuclear modes per site as their frequency does not influence the hopping rate. Coupling with quantum modes can be introduced but this would increase the number of model parameters, something undesirable in this phenomenological study but fairly easy when specific chemical systems are considered (because such parameters can be computed). Finally, while the electron-phonon coupling parameter g is likely to be different between even and odd sites (i.e. for different monomers), only one of the two monomers will generate the states relevant for transport in one of the two bands, so it is unnecessary to introduce two electron-phonon coupling parameters. If the charge carrier localization is largely determined by the static disorder in H_0^{el} , then one can describe the transport as a sequential hopping between the eigenfunctions of H_0^{el} where $V^{el-nucl} + V^{el}(t)$ are included as small perturbations. This latter assumption is in agreement with the current consensus view^[7, 10] but, as we will point out below, it is not guaranteed to be always valid. When it is valid, a master equation can be derived for the hopping rates between eigenstates of H_0^{el} , which can be used to evaluate the mobility along the polymer chain following the procedure detailed in ref. ^[17] and outlined here. The hopping rate between eigenstates of H_0^{el} is given by an expression reminiscent of (but distinct from) Marcus equation for electron transfer:

$$k_{j \rightarrow k} = \frac{G^2 S_{jk}^2}{\hbar} \sqrt{\frac{\pi}{\lambda_{j \rightarrow k} k_B T}} \exp \left(-\frac{(\lambda_{j \rightarrow k} + E_k^0 - E_j^0)^2}{4 \lambda_{j \rightarrow k} k_B T} \right) \quad (5)$$

In (5), instead of the explicit electronic coupling between initial and final states, we have the product of the fluctuation of the inter-monomer coupling G^2 times the squared overlap between the unperturbed wavefunctions $S_{jk}^2 = \sum_i (c_{j,i}^0 c_{k,i+1}^0)^2 + (c_{j,i}^0 c_{k,i-1}^0)^2$, i.e. the non-adiabatic coupling instead of the electronic coupling of Marcus theory. The reorganization energy of the hopping process $\lambda_{j \rightarrow k}$ can be expressed as $\lambda_{j \rightarrow k} = \frac{g^2}{m\omega^2} \sum_i |c_{ji}^0|^4 + |c_{ki}^0|^4$ i.e. it decreases as the states become more delocalized. In ref. ^[17] we derived the condition for the validity of eq. (5) as $G / \lambda_1 < \sigma_\beta / \beta$, which is generally satisfied for most realistic situations and it is distinct from the condition discussed in the introduction (and further below) that the disorder is more important than the electron-phonon coupling in determining the localization. The condition implies that one cannot use this model in the limit of vanishing disorder σ_β where the transport would become coherent.

The mobility is computed in the simplified limit of a small field F applied along the length of the polymer which modifies all energy differences $E_k^0 - E_j^0$ by an additive term $-eR_{j \rightarrow k}F$, where $R_{j \rightarrow k}$ is the position difference between initial and final state. For the master equation in the low charge density limit, $\dot{p}_j = -\sum_{j \neq k} k_{j \rightarrow k} p_j - k_{k \rightarrow j} p_k$, the steady states solution $\{p_j^S\}$ is found as the eigenvector corresponding to null eigenvalue of the matrix of the rates. The mobility is then computed as $\mu = \frac{1}{n \cdot F} \sum_j \sum_k k_{j \rightarrow k} p_j^S R_{j \rightarrow k}$ where n is the charge density.^[21]

The logarithm of the mobilities of 1-D chains are distributed normally when different realizations of disorder are considered (shown in SI) and we therefore report the geometric average of the mobility (30 evaluations per data point) in the limit of vanishing field ($|eR_{j \rightarrow k}F|$ typically much smaller than $|E_k^0 - E_j^0|$) and carrier concentration. The bulk mobility is determined by the interplay between intra- and inter- molecular transport ^[22] and the polymer chain geometry^[23]. For example it has been shown that the charge diffusivity is determined only by intra-chain hopping (for rigid rod polymers) and by a combination of intra- and inter-chain hopping (for very flexible chains).^[23] We consider explicitly only the intra-chain transport because only in this case the chemically controllable parameter Δ has two competing effects (reducing the intra-chain coupling but also the activation energy for transport). The inter-chain transport simply becomes less dispersive (faster) for larger values of Δ (narrower bands), which reduce the activation energy, and is determined by the inter-chain coupling, a parameter that is much smaller than the polymer bandwidth and unrelated to it. A non-vanishing field would make the results strongly dependent on the conformation of the chain as it is known that kinks in the polymer chain can become traps for the carrier if the field is strong in comparison with the disorder,^[22] an effect that we do not wish to

investigate here but that could be included. The results are discussed as functions of the disorder (σ_β / β) and of the difference between on-site energies (Δ / β). The other parameters, which do not affect the conclusion of this work, are similar to those used in ref. ^[17], where a broader justification based on computational data is provided and the scaling of the results with the model parameters is discussed. They have been set as follows: $G = 0.01$ eV, $k_B T = 0.025$ eV, $g^2 / m\omega^2 = 0.45$ eV, $\beta = 1.0$ eV.

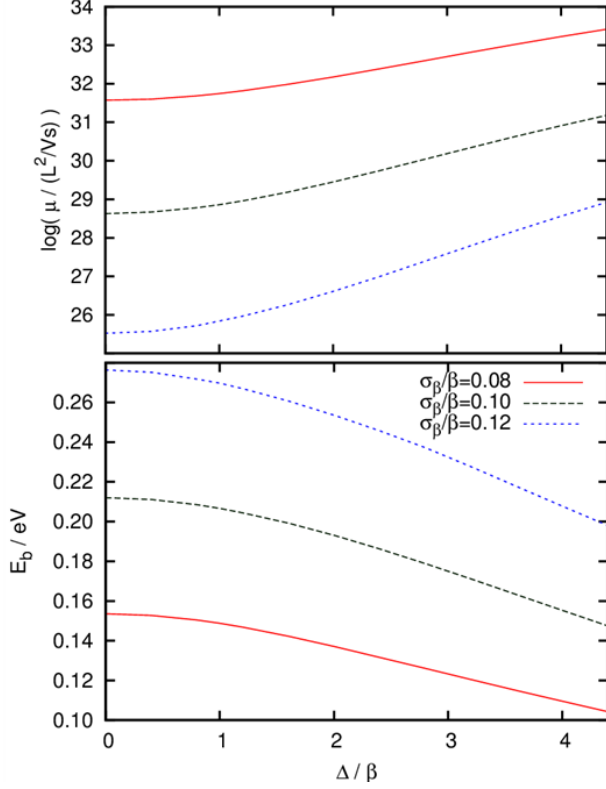


Figure 2. (top) Increase of the mobility with increasing difference between on-site energies Δ for different values of static disorder. (bottom) Corresponding decrease of the activation energy E_b computed from the temperature dependent mobility (see SI).

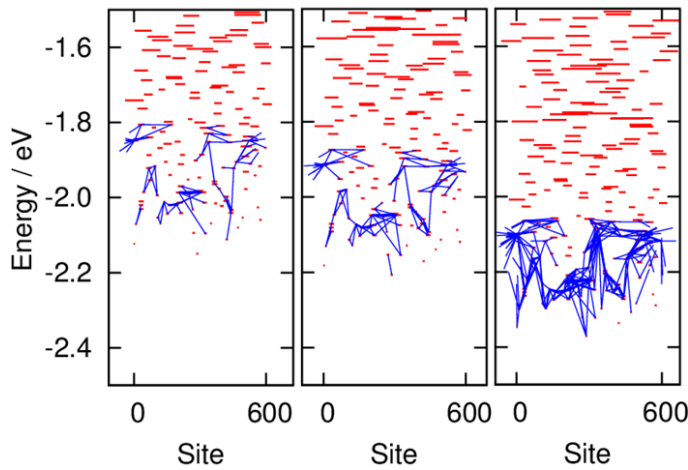


Figure 3. Diagram representing the energy levels (horizontal red segments) and their delocalization (length of the segment) for $\Delta/\beta = 0, 1, 2$ (left, centre, right panel) in a system with 600 sites. The blue segments connect sites with particle currents exceeding a common threshold. Increasing delocalization at higher energy is evident from the diagram. The larger total particle current for $\Delta/\beta = 2$ is due to the presence of more delocalized states near the bottom of the band.

Figure 2(top) illustrates how the mobility increases moderately with increasing Δ , i.e., how band narrowing is not detrimental to mobility. The model predicts a mobility that follows the simple Arrhenius law ($\mu \approx \mu_0 \exp(-E_b/k_B T)$), shown in the SI), which is used to define an empirical activation energy E_b . Figure 2(bottom) shows how the activation energy decreases with the increase of Δ and that the decrease of the band width is responsible for the overall increase of mobility with increasing Δ . The effect can be visualized as in Figure 3, where the highest particle currents are shown for systems with different values of Δ . When Δ is increased, the lower band gap and the smaller band width cause more delocalized states to be energetically closer to the band edge, allowing more long range hopping. As the increase of mobility with Δ is not large compared to the variability in mobility that one can observe in these materials, a fair interpretation of the results is that an increase in Δ makes the material more insensitive to the local disorder: the same local disorder generates deeper traps in wider-band (small Δ) materials.

To make the results more easily comparable with other theories and experiments we note that a mobility $\log(\mu/(L^2/Vs)) = 29$, i.e. the center of the mobility range in Figure 2(top), corresponds to an absolute mobility of $0.04 \text{ cm}^2/Vs$ if the distance between monomers L is set to 1 nm and the vertical range of the figure would span between 10^{-3} and $6 \text{ cm}^2/Vs$. The model, by design, captures the experimental range between moderate and high mobilities because it does not include the possible effect of extrinsic defects. It should not be forgotten that co-polymers, having generally a smaller band gap, are less sensitive to the presence of extrinsic defects and this also contributes to their high mobility.^[24]

An essential feature of this model is that the master equation was derived from the microscopic Hamiltonian and not imposed from the outset as in the vast majority of phenomenological models.^[25] This allowed the inclusion of variable delocalization of states and hopping rates consistent with the electronic structure of the material. Having started from the Hamiltonian rather than the master equation it is also possible to establish the limit of validity of our result. If we increase indefinitely Δ , the bandwidth will eventually vanish and the assumption that the charge localization is mainly due to the polymer disorder becomes invalid. With vanishing bandwidth the system will form small polarons, localized on a single monomer.^[26] When the bandwidth is of the order of the polaron formation energy of a single monomer (typically between 0.1 and 0.5 eV^[27]) the transport is more appropriately described by small polaron hopping and is likely to be less efficient than the transport involving delocalized states. One can therefore argue that the electronic structure of the co-polymer is beneficial to charge transport as long as the bandwidth remains larger than the polaron formation energy. Even more intriguingly, it is possible that the highest possible mobility achievable for disordered polymers is found for those materials whose band is narrow

enough to minimize the activation energy for transport but not as narrow to promote the formation of very stable small polarons. To illustrate this in figures, we can consider the case where $\Delta/\beta = 2$, the bandwidth is close to β (Figure 1), and $\lambda \sim \beta$ would be a situation where this maximum mobility can be achieved and that corresponds to the plausible value of $\beta \sim 0.4$ eV. While still not fully conclusive, there is some computational and experimental evidence that the highest mobility amorphous polymers are found in a transport regime where small polarons start becoming important.^[28]

In conclusion, we have shown that, at a constant level of disorder in the electronic Hamiltonian, the narrower bands present in a semiconducting co-polymer are overall beneficial to transport, i.e. the weaker coupling between states is more than compensated by a lower activation energy for transport. This is true until the band is so narrow that small polarons are formed on each monomer. It is essentially impossible to predict the level of disorder of any new polymer but it is relatively easy to compute and predict the bandwidth and the electron-phonon coupling for a given compound. The proposed model suggests that it is possible to select the parameters that can be controlled (coupling and electron-phonon coupling) to place the polymer in a region of the parameter space where the disorder (uncontrollable) plays a lesser role. In the perspective of going toward more realistic models, it is also easy to avoid some of the simplifications introduced in this model (presence of a single classical nuclear mode, a single electronic state per monomer) when the additional needed parameters can be derived from atomistic models.

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